is between ordered structures.

(2) A new surface feature is observed from the $(\sqrt{2}\times\sqrt{2})R45°$ structure, at $\vec{k}_{\parallel}=(\pi/a,\pi/a)$, 1.4 eV below E_F, which is attributed to umklapp and surface photoemission from a state associated with a bulk band edge at $\bar{\Gamma}$.

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Do Metal Alloys Work as Substrates for Surface-Enhanced Raman Spectroscopy?

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Surface-enhanced Raman signals are reported from pyridine adsorbed onto $Ag_{1-x}Pd_x$ for $x \lesssim 0.04$. For $x \gtrsim 0.05$ the alloys do not support enhancement within our limit of detection. The quenching is due to the introduction of Pd *d* states which are involved in electron excitations that interfere with Ag's favorable free-electron–like behavior.

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The occurrence of an anomalously large Raman-scattering cross section associated with adsorbed molecules has been restricted to only a few metals. The relationship between the enhancement and substrate properties must be understood before surface-enhanced Raman scattering (SERS) can be exploited to study the vibrational structure of adsorbates. Previously, only Ag, Cu, and Au were reported[1] as unambiguously supporting the enhancement at a level which allows experimental detection.

We report here the first observation of SERS on an alloy surface. We have detected Raman scattering from pyridine adsorbed onto Ag-Pd alloys under electrochemical control with Pd concentration as high as 4% (0%, 1%, 2%, and 4%). The alloy surfaces provide a significantly improved catalytic function in hydrogen adsorption and are expected to affect many other reactions in a similar manner. Surface enhancement, if present, on Ag-Pd alloys with Pd > 5% (5%, 10%, 20%) is smaller than our ability to detect it by use of incident photon wavelengths of 4579, 4880, or 5145 Å. We attribute this quenching to the introduction of low-energy excitations which supply damping channels to the normally free-electron-like characteristics of Ag.

Our electrochemical technique involved encapsulating four polycrystalline samples, Ag and three alloys with different Pd concentrations, side by side but electrically isolated from each other in Teflon so that equal sample areas (2 mm × 4 mm) were exposed to the solution (either KCl or Na_2SO_4 at $0.1M$ concentration plus 50 mM of pyridine). Four separate electrical leads were brought out the back of the mount through a watertight seal. All four samples received identical mechanical polishing by use of 600-grit SiC and 1-μm Al_2O_3 followed by an ultrasonic rinse in high-purity water (distilled four times). Oxidation-reduction cycles were not used to clean and roughen the surface. The pure Ag sample was subjected to the identical heat treatment as were the alloys to reduce hardness differences. Scanning electron microscopy with a 200-Å resolution on these surfaces revealed identical surface topographies (polishing grooves ~500–1000 Å across) independent of the Pd concentration. With use of a glove bag, the mount was then immediately introduced into the electrochemical chamber, which had been purged with N_2. The fixture onto which the mount was attached was designed so that the sample mount could be accurately translated strictly parallel (within 0.002 in.) to the sample surfaces to bring each sample into the laser beam, one at a time. The s-polarized incident light from an argon laser (100–180 mW) was focused to a spot on the sample under test at an angle of 60° from the surface normal. The collection lens (f/1.8) was arranged for detection along the surface normal so that the sample was imaged onto the entrance slit (set at 400 μm) of the Jarrell-Ash Model-25-400 double monochromator.

Surface segregation does not occur when Ag-Pd alloys are abraded under high-vacuum conditions.[2] The pure metals are also quite similar electrochemically, and so no additional segregation driving force is expected when the alloy surfaces are under voltage control. We detected no composition difference, as measured by depth-profiled Auger-electron spectroscopy, between 10% Pd alloys, which had been abraded with 600-grit SiC in air, and identical samples which had additionally been electrochemically polarized in our sample chamber for 5 min at -0.6 V.

In an additional test to confirm that the alloy surfaces contained Pd concentrations representative of the bulk material, we measured the hydrogen reduction current versus applied voltage on each of the four samples in turn. In our solution, with pH = 8.3, the hydrogen reduction reaction involves breaking a bond in H_2O to produce adsorbed hydrogen. The hydrogen reaction rate, at a given applied voltage, is a measure of the catalytic behavior of the metal surface toward this step. On the alloy surfaces, the hydrogen reaction rate is a measure of the surface concentration of Pd to Ag. The results of the latter test are shown in Fig. 1. The trend, shown here as a decreasing activation energy for the hydrogen reaction, continued throughout the alloy series we investigated (0% to 20% Pd). If extensive surface segregation of Pd were responsible for our Raman-scattering results, we would not have observed such a sensitive and progressive dependence of the hydrogen reduction activation energy on the bulk Pd concentration as is demonstrated in Fig. 1.

Because of the localization of the interfacial voltage drop, we can isolate the Raman signal associated with pyridine which is within 25 Å of the metal by concentrating on voltage-induced intensity changes. A typical trial consisted of ten averaged spectra from 1180 to 1260 cm^{-1} on each of the four samples and at each of two applied voltages. Information was recorded in a variety of sequences to verify that changes among the samples were reproducible, were not due to any time dependence, and that the voltage-induced changes were reversible.

Figure 2 contains the Raman-scattering data as recorded from alloys containing 0%, 2%, 4%, and 5% Pd with two different applied voltages. We emphasize again that only mechanical abrasion was used to prepare the surfaces and that

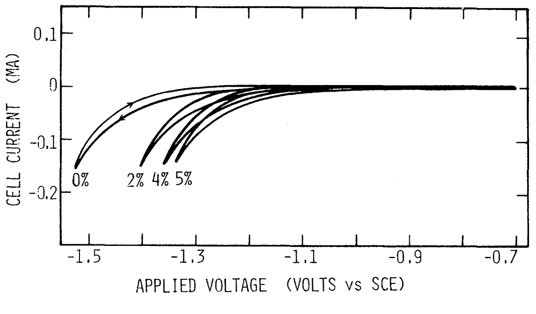

FIG. 1. Current through the samples vs applied voltage as a function of percent Pd concentration. $0.1M$ KCl + $0.05M$ pyridine; 20 mV/sec. The progressively lower activation voltage for current flow into the hydrogen reduction reaction with increasing Pd concentration is an indication that the surface Pd concentration is close to that of the bulk.

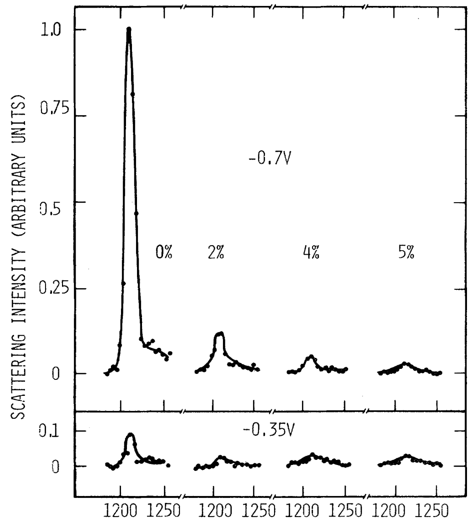

FIG. 2. Raman signals from the 1215-cm^{-1} mode of pyridine on mechanically abraded $Ag_{1-x}Pd_x$ samples. Differences between the two applied voltages represent that contribution coming from pyridine located within 25 Å of the surface.

conditions which would have lead to surface segregation were strictly avoided. The enhancement on pure silver is much larger at -0.7 versus s.c.e. (saturated calomel electrode). A voltage-dependent peak is also detectable for Pd concentrations of 2% and 4% but is absent for the 5%, 10%, and 20% Pd samples. We estimate that the Raman-scattering enhancement factor must be lower than about 2000 to escape detection in our system.

The most probable explanation of the alloy effect is associated with the influence that Pd has on the electronic density of states and thereby on the optical properties of Ag. X-ray–photoemission–spectroscopy data have revealed a broad *d* level centered about 2 eV below the Fermi level in dilute Ag-Pd alloys.[3] This gives rise to additional electronic excitations at energies well below the onset for interband transitions in pure Ag (3.9 eV). The complex dielectric function, ϵ, for dilute Ag-Pd alloys has been determined earlier by Schmidt and Lynch,[4] and can be used to analyze the role of the Pd *d* level in modifying optical parameters which enter the various theoretical models for SERS.

Table I lists the values of ϵ vs Pd concentration in a range which covers the conditions where SERS is experimentally undetectable. Note how $\mathrm{Im}\,\epsilon$ increases by nearly an order of magnitude moving down the table. This reflects the added dissipation which the Pd *d* states introduce.

The optical properties of the surface are central to electrodynamic theories in which the high-frequency screening character of the metal plays a role.[5] These models include the image-field models, the surface-induced molecule resonance models, and most of the recently proposed metal-particle resonance models. A function which appears in all of these theories, in a nonlinear way, is $\gamma = (\epsilon - \epsilon_0)/(\epsilon + a\epsilon_0)$, where ϵ_0 is the real optical dielectric constant of the electrolyte, and a is a geometrical factor ($a = 1$ for a plane, or 2 for a sphere, for instance). Table I shows how γ (for $a = 2$) changes when Pd is introduced. The most obvious trend is the significant increase in $\mathrm{Im}\gamma$. Large $\mathrm{Im}\gamma$ values are detrimental in all the electrodynamic theories although quantitative differences depend on the details of such things as surface geometry and the distance of the molecule from the metal.

A special case where electrodynamics enters the theory is one in which surface plasmons act as the optical resonance. The relaxation time for surface-plasmon decay to single-particle excitations can be calculated[6] from $\tau = [\epsilon_1(\epsilon_1 + \epsilon_0) + \frac{1}{2}\omega\, d\epsilon_1/d\omega][\omega\epsilon_2]^{-1}$, where $\epsilon = \epsilon_1 + i\epsilon_2$. The last column in Table I shows how rapidly τ decreases

TABLE I. The effect of Pd concentration on electrodynamic parameters of $Ag_{1-x}Pd_x$ alloys at 514.5 nm.

x	ϵ	γ [a]	τ (10^{-15} sec) [a]
0	$-11.025 + i0.4454$	$1.7069 + i0.0421$	65.6
0.024	$-9.937 + i0.9218$	$1.8132 + i0.1172$	25.4
0.042	$-9.562 + i1.2988$	$1.8425 + i0.1817$	16.5
0.07	$-9.607 + i2.2720$	$1.7676 + i0.2874$	9.53
0.148	$-8.684 + i4.0205$	$1.6408 + i0.5009$	4.24

[a] Calculated from ϵ of first column with $\epsilon_0 = 1.77$.

with increasing concentrations of Pd. It is clear that even dilute Ag-Pd alloys will not support surface-plasmon resonances as well as pure Ag.

Even the theories which involve the direct excitation of electron-hole pairs as the primary step in SERS are adversely affected by the introduction of damping. In the alloys, damping channels would compete with the Raman-scattering processes for energy which was initially deposited in the electron-hole excitation spectrum.

Our results illustrate, by the controlled introduction of decay channels, how necessary it is for SERS substrates to have undamped free-electron–like characteristics (large negative ϵ_1, very small ϵ_2). This partially explains the metal and incident-energy dependence exhibited by Cu, Ag, and Au. The situation is complicated by geometrically defined surface resonances which introduce additional incident-energy effects. The combination of the two effects have given rise to some confusion surrounding the true incident-energy dependence of SERS.[7]

In summary, we have shown that surface-enhanced Raman scattering can be observed on dilute Ag-Pd alloys, provided that the Pd concentration is below 5%. For more concentrated alloys the enhancement is quenched because of the introduction of effective decay channels involving electron excitations between the Pd *d* states and the Fermi level. Other materials where similar excitations are probable are also predicted to be unfavorable substrates for SERS.

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